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A facile strategy for the synthesis of guanidinium-functionalized polymer as alkaline anion exchange membrane with improved alkaline stability

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ABSTRACT

A facile strategy for the synthesis of guanidinium-functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with improved alkaline stability was developed by the reaction of bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) with 2-benzyl-1,1,3,3-tetramethylguanidine (BTMG). The chemical structure of guanidinium-functionalized polymers was confirmed by ^1H NMR and FT-IR spectroscopy. A crosslinked membrane of the polymer which have an ionic exchange capacity (0.80 mmol/g) and low swelling ratio ($< 15\%$) was fabricated. The ionic conductivity of the cross-linked membrane was higher than $1.0 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature and $5.1 \times 10^{-2} \text{ S cm}^{-1}$ at 70°C . The microstructure of hydrophobic/hydrophilic phase separation of the film was observed by transmission electron microscopy (TEM). Finally, the alkaline stabilities of model guanidiniums and the cross-linked membrane were evaluated respectively. The results showed that the bulky guanidinium cation exhibited higher alkaline stability due to the steric hindrance of the substituents, and the cross-linked membrane remain the ionic conductivity of $4.2 \times 10^{-2} \text{ S cm}^{-1}$ at 70°C after being immersed in 1 M NaOH/D₂O solution at 60°C for 2 days. The mechanical properties of the membranes were also measured before and after 2 days of stability testing. All results suggest that this alkaline anion exchange membrane (AAEM) functionalized by bulky guanidinium groups could be considered as a promising candidate for polymer electrolyte membrane in alkaline fuel cells.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) has been recognized as a promising alternative energy source due to its higher energy conversion efficiency and environmentally friendliness. As a key component in PEMFCs, proton exchange membranes (PEMs) are currently based on perfluorosulphonic acid polymers, such as Nafion by DuPont Company, which possess high ionic conductivity, excellent mechanical properties, high chemical stability, and long-term durability [1–3]. Unfortunately, PEMFCs still have some drawbacks which prevent their applications, such as high fuel crossover, slow electrode kinetics, and the use of noble electrocatalysts. Alkaline anion exchange membrane (AAEM) fuel cells, using hydroxides as conductive ions instead of protons in PEMFC, has received much attention, because they can potentially overcome the above mentioned hurdles in the PEMFCs. Under alkaline condition, the kinetics of both oxygen reduction and fuel oxidation

can be enhanced, and more importantly, non-noble metals (silver or nickel) can be used as electrocatalysts. In addition, different from alkaline fuel cell with liquid electrolyte, the introduction of solid AAEM can mitigate the electrolyte leakage and carbon dioxide poisoning during long-term use [4–7].

Various quaternary ammonium-functionalized polymers have been used as the materials for fabricating AAEMs, such as quaternized polysulfones [8,9], poly(phenylene) [10], poly(phenylene oxide) [11,12], poly(methyl methacrylate-co-butyl acrylate-co-vinylbenzyl) [13,14], and radiation-grafted fluorinated polymers [15,16]. However, at present these polyelectrolytes based on quaternary ammonium groups still suffer from some defects, including low ionic conductivity and poor alkaline stability especially at elevated temperature. Since the properties of polymer membranes are closely related to the structure and composition of polymers, it is very important to design and synthesize new types of polymers with high ionic conductivity and alkaline stability. Coates et al. [17] fabricated hydroxide-conducting thin films through ring-opening metathesis copolymerization of a tetraalkylammonium-functionalized norbornene with a crosslinker (dicyclopentadiene). The results showed that the film possessed high alkaline stability due to the lack of β -hydrogen atoms

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in the ammonium groups. Besides quaternary ammonium polymers, some new kinds of cationic polymers with different functional groups, such as imidazolium [18–20], phosphonium [21,22], benzimidazolium [23] and sulfonium [24] cations have been reported in the preparation of AAEMs.

Guanidine groups exist in a variety of natural products and are often incorporated into synthetic organic compounds or polymers, which have many applications in biological, medicinal fields, and organic synthesis, especially asymmetric synthesis [25]. In comparison with quaternary ammonium hydroxide, quaternary guanidinium hydroxide combines stronger basicity and higher alkaline stability due to the significant delocalization of positive charge over guanidinium group [26]. Therefore, it is advantageous to use the guanidinium as the functional cation for designing new AAEM with high ionic conductivity and alkaline stability. Zhang et al. [27] firstly reported a novel alkaline anion exchange membrane composed of poly(arylene ether sulfone) containing pendant quaternary guanidinium groups, which exhibits high hydroxide conductivity and outstanding alkaline stability. Kim and coworkers prepared phenyl-guanidinium functionalized poly(arylene ether sulfone) using activated aromatic fluorine atoms, followed by methylation [28].

Until now, the guanidinium-functionalized polymers are usually prepared by the quaternization of chloromethylated or bromomethylated aromatic polymers with penta-substituted guanidines, such as 1,1,2,3,3-pentamethylguanidine (PMG). We notice that the synthesis of PMG involves the reaction of dry methylamine gas with Vilsmeier salt under dry condition, because Vilsmeier salt is very sensitive to moisture. Moreover, Vilsmeier salt is often prepared by reaction of urea with some highly toxic and environmentally detrimental chemicals, such as oxalyl chloride, phosphorus oxychloride, and thionyl chloride [27,29–31]. Therefore, it is highly desired to develop a facile strategy for the preparation of guanidinium-functionalized polymers.

In this paper, a new facile approach has been developed for the synthesis of a penta-substituted guanidine (2-benzyl-1,1,3,3-tetramethylguanidine, BTMG), using commercial available 1,1,3,3-tetramethylguanidine (TMG) and benzyl chloride. Based on this new method, a guanidinium polymer, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing 2,2-bis(benzyl)-1,1,3,3-tetramethylguanidinium groups was prepared, by the reaction between bromomethylated PPO and BTMG. Finally, a crosslinked membrane was obtained by the solution-casting method and heat treatment. And the morphology and properties of this membrane were investigated.

2. Experimental

2.1. Materials

1,1,3,3-Tetramethylguanidine (TMG) was purchased from Zibo Gelin Aipu chemical Co., Ltd, China. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was obtained from the Institute of Chemical Engineering of Beijing (China), and its molecular weight is 90,000 g/mol. N-bromosuccinimide (NBS) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. 2,2'-Azo-bis-isobutyronitrile (AIBN) was recrystallized from methanol twice. All other chemical agents were used as received unless otherwise noted.

2.2. Synthesis of 2-benzyl-1,1,3,3-tetramethylguanidine (BTMG)

First, 1,1,3,3-tetramethylguanidine (TMG) (30 mL, 237.0 mmol) was placed in a 250 mL round-bottom flask, and then benzyl chloride (3 mL, 26.07 mmol) was added dropwise to the solution via a dropping funnel. After stirred for 24 h at room temperature,

the mixture was filtered. The filtrate was dissolved with 50 mL of ethyl ether, and then washed successively with distilled water (4 × 50 mL), and dried over anhydrous Na₂SO₄. By evaporating the solvent, a brown oil product was obtained in 40% yield. ¹H NMR: δ (CDCl₃, ppm) 7.42–7.16 (m, 5H), 4.40 (s, 2H), 2.78 (s, 6H), 2.74 (s, 6H). ¹³C NMR: δ (CDCl₃, ppm) 160.9, 143.7, 128.0, 127.1, 125.8, 53.0, 39.7, 38.9.

2.3. Synthesis of 2,2-bis(benzyl)-1,1,3,3-tetramethyl guanidinium (BBTMG) bromide

The model guanidinium compound of BBTMG was synthesized as follow. BTMG (0.7803 g, 3.800 mmol) was dissolved in 5 mL toluene, and benzyl bromide (0.45 mL, 3.800 mmol) in 5 mL toluene was added dropwise into the solution. The mixture was stirred for 24 h at room temperature, and then the precipitate was filtered, washed with diethyl ether and dried in a vacuum at room temperature. The product was obtained with a yield of 95%. ¹H NMR: δ (CDCl₃, ppm) 7.40–7.22 (m, 10H), 4.33–3.87 (m, 4H), 3.16–2.95 (m, 12H). ¹³C NMR: δ (CDCl₃, ppm) 162.8, 134.1, 129.3, 128.9, 53.8, 41.2, 40.5.

2.4. Synthesis of 2-benzyl-1,1,2,3,3-pentamethyl guanidinium (BPMG) iodide

BTMG (0.6524 g, 3.178 mmol) was dissolved in 10 mL toluene and CH₃I (0.16 mL, 3.178 mmol) was added into the solution. The mixture was stirred for 24 h at room temperature, and then the precipitate was filtered, washed with diethyl ether and dried in a vacuum at room temperature. The product was obtained with a yield of 97%. ¹H NMR: δ (DMSO-d₆, ppm) 7.45–7.33 (m, 5H), 4.65–4.08 (m, 2H), 3.08–2.64 (m, 15H). ¹³C NMR: δ (DMSO-d₆, ppm) 162.4, 135.3, 128.8, 128.2, 127.6, 55.2, 37.5.

2.5. Synthesis of bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO)

Bromination reaction of methyl groups on PPO was performed according to the literature [32]. After PPO, NBS and AIBN were dissolved in chlorobenzene, the mixture was stirred under refluxing for 4 h, and then the reaction solution was precipitated into a 10-fold excess of methanol. The brominated polymer was obtained by filtrating, reprecipitating into ethanol two times, and drying in a vacuum at 50 °C. Bromination ratio of the methyl groups was calculated from ¹H NMR spectrum of BPPO.

2.6. Synthesis of PPO containing quaternary guanidinium bromide

To a solution of BPPO (0.713 g, 2.303 mmol of –CH₂Br) in dimethylformamide (20 mL), BTMG (0.565 g, 2.752 mmol in 10 mL DMF) was added and stirred at 80 °C for 24 h (the molar ratio of BTMG to bromomethyl group in BPPO is 1.2). After the mixture was cooled to room temperature, the guanidinium bromide-functionalized PPO (BPPO/G[Br]) was obtained by removing the solvent and subsequently precipitated into large amount of diethyl ether. The polymer was dried under reduced pressure at 40 °C for 12 h.

2.7. Membrane preparation

BPPO/G[Br] was dissolved in dimethylformamide (10 wt%), and cast on a flat glass plate. And then a crosslinked membrane was obtained after evaporation of the solvent at 40 °C for 6 h, 60 °C for 12 h, and 120 °C for 24 h in a vacuum.

In order to exchange bromide ion for hydroxide ion, the crosslinked membrane of BPPO/G[Br] was immersed in 1 M NaOH

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